the insulator which can be taken as

$$N(\epsilon)=4\pi/(2m/h^2)^{3/2}[\epsilon-(\varphi_0-\Delta\varphi)]^{1/2}.$$

Integrating (5) we get

$$n_0=2\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\exp(-\varphi/kT)\exp(\beta E_0^{1/2}). \quad (6)$$

Substituting (6) into (4) we arrive at

$$J=2e\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\mu E_0\exp(-\varphi/kT)\exp(\beta E_0^{1/2}). \quad (7)$$

Eq. (1) and (7) are incompatible, but differ only by the pre-exponential factor. The J-V characteristic will be determined by which of the two equations is the limiting case; and this is (5) as can be seen by evaluating the pre-exponential terms for $T=300°\mathrm{K}$ in each of the equations; thus

$$J=1.08\times10^7\exp(-\varphi/kT)\exp(\beta E_0^{1/2})\ \mathrm{A/cm^2}, \quad (1)$$

$$J=1.6\mu E_0\exp(-\varphi/kT)\exp(\beta E_0^{1/2})\ \mathrm{A/cm^2}. \quad (7)$$

Assuming $\mu=10$, it will be seen that fields of 10^6 V/cm are required before (1) becomes the limiting mechanism.

At $E_0=0$, i.e., the transition field, J in (7) becomes zero. This does not mean, of course, that the current through the system is zero. This condition corresponds to the virtual cathode being at the cathode-insulator interface, the current being carried across the interface solely by the diffusion process. However, for fields slightly in excess of the transitional field the diffusion current becomes negligible compared to the field current.

It will be noted that there is no clear distinction in this case between the bulk-limited and electrode-limited processes, because each plays a part in the conduction process. The density of the free carriers at the interface is electrode limited [see Eq. (5)], while the mobility, which determines the velocity, is a bulk property.

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[1] A. J. Dekker, Solid State Physics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1957), pp. 220-226.

PHONON-COUPLED PAIR SPECTRA OF K_2ReCl_6 IN SINGLE CRYSTALS OF K_2PtCl_6†

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The optical spectra of dilute single crystals of K_2PtCl_6 containing Re^{+4} show absorption peaks which may be assigned to ion pairs of Re^{+4} in addition to lines arising from the single ion. The diamagnetic cubic crystal, K_2PtCl_6, has an antifluorite, face-centered structure in which Re^{+4} readily substitutes for the platinum ion. In a cubic environment the rhenium ground-state configuration, $t_{2g}{}^3$, forms orbital states which transform like the ${}^4A_{2g}$, ${}^2E_g$, ${}^2T_{1g}$, and ${}^2T_{2g}$ representations of the cubic group. Under spin-orbit interaction, further removal of degeneracy occurs to give states which transform like Γ_6, Γ_7, and Γ_8 of the double group, which are two-fold degenerate except for Γ_8 which is four-fold degenerate. The spectrum reported in this note arises from the free-ion transition from ${}^4A_{2g}$ (Γ_8) to ${}^2T_{2g}$ (Γ_7) and the associated pair transitions.

The group theory of the vibration spectrum of this crystal structure has been considered by Pollock.[1] He has shown that there are three odd modes of the chloride ions relative to the rhenium ion in addition to the reststrahlen modes of K^+ moving with respect to the $ReCl_6{}^=$ complex. The three modes of the complex transform like Γ_{4u}, Γ_{4u}, and Γ_{5u} and will be given the usual notation of ν_3, ν_4, and ν_6, respectively. Woodward and Ware[2] have shown that ν_3 is about 313 $\mathrm{cm^{-1}}$ and ν_4 is 172 $\mathrm{cm^{-1}}$ at room temperature. Recently it has been shown that ν_6 is 124 $\mathrm{cm^{-1}}$ at 4.2°K.[3]

At 4.2°K, a 5% Re in K_2PtCl_6 crystal shows four relatively intense narrow lines which are assigned to the electronic transition[4] ${}^4A_{2g}$ (Γ_8) $\rightarrow{}^2T_{2g}$ (Γ_7) coupled with o-o, ν_6, ν_4, and ν_3 vibration modes. In addition, resolved fainter lines are observed near the o-o and ν_3 absorptions as shown in Figs. 1 and 2. An unresolved broadening near ν_4 is observed, but no additional lines are clearly evident near ν_6.

The faint lines near the o-o transition are

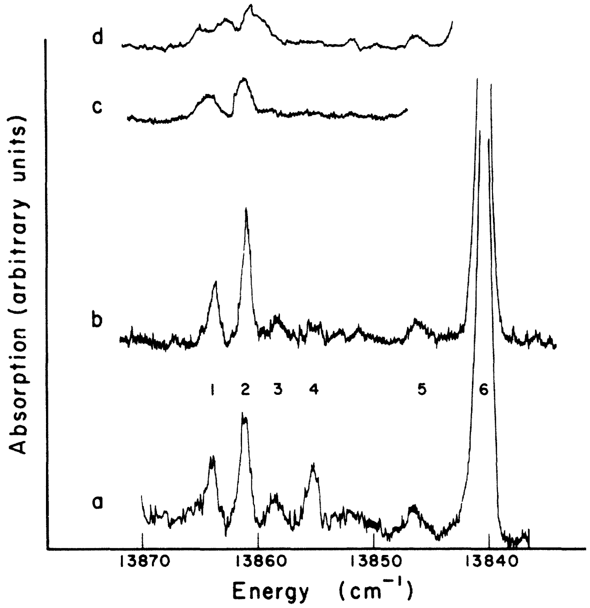

FIG. 1. A copy of the densitometer tracings of the *o*-*o* absorption spectrum. The numbering scheme of the absorption corresponds to that of Table I. (a) $T = 4.2°\mathrm{K}$, $H = 0$ G; (b) $T = 1.5°\mathrm{K}$, $H = 0$ G; (c) $T = 1.5°\mathrm{K}$, $H = 5.0$ kG; (d) $T = 1.5°\mathrm{K}$, $H = 10.0$ kG.

assigned as pair spectra for the following reasons:

(a) If the temperature is lowered to 1.5°K, the intensities of all but the two highest energy lines, 1 and 2, near the *o*-*o* single-ion absorption are diminished as shown in Fig. 1(b). Lines 1 and 2 must be transitions from the ground state only.

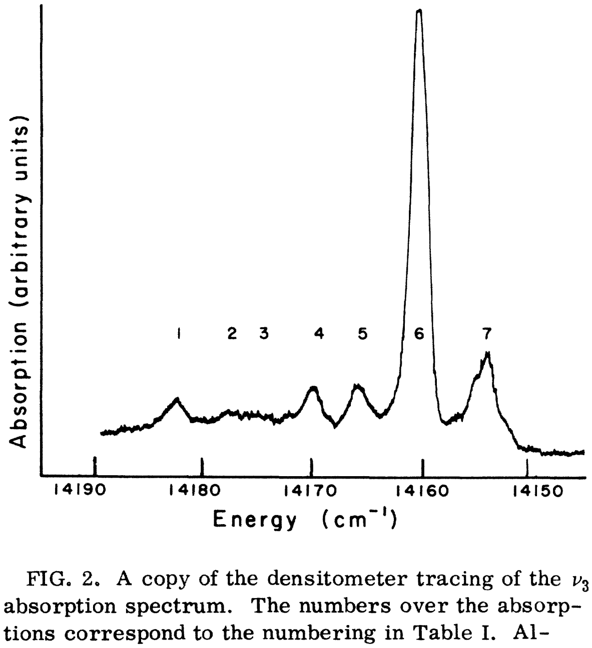

FIG. 2. A copy of the densitometer tracing of the ν_3 absorption spectrum. The numbers over the absorptions correspond to the numbering in Table I. Although the tracing does not clearly show lines 2 and 3, they are readily evident in the photographic plate.

(b) The spectrum of a crystal containing 1% rhenium at $T = 4.2°\mathrm{K}$ shows no detectable lines near the *o*-*o* single-ion line.

(c) If the assumption is made that the faint lines are pair spectra, the energy differences may be calculated from the Heisenberg exchange Hamiltonian, $\mathcal{H} = -2Js_1 \cdot s_2$, where J is the isotropic exchange parameter. For the ground state $s_1 = s_2 = \frac{3}{2}$ whereas for the excited state $s_1 = \frac{3}{2}$ and $s_2 = \frac{1}{2}$, since the single-ion spectrum corresponds to a transition to a doubly degenerate state. The ground-state energies are $(+15/2)J$, $(+11/2)J$, $+\frac{3}{2}J$, and $(-\frac{9}{2})J$, and the excited state energies are $\frac{5}{2}J'$ and $-\frac{3}{2}J'$, where the prime denotes the excited state.

If it is assumed that $\Delta S = 1$ transitions are the most intense and all transitions are modified by a Boltzmann factor, the *o*-*o* pair spectrum shown in Fig. 1 may be fitted with $J = -2.91\ \mathrm{cm}^{-1}$, $J' = -0.66\ \mathrm{cm}^{-1}$. The root-mean-square deviation of the observed pair energies from the calculated energies is $0.17\ \mathrm{cm}^{-1}$. Table I lists the observed energies, the observed energy differences, and the calculated energy differences using these parameters. It is found that the position of the free-ion absorption is consistent with these assignments.

The readily apparent faint lines near the ν_3 transition are interpreted as pair spectra associated with transitions from the ground state, $S = 0$, to a phonon-coupled excited state. The reasons for this assignment are the following: (a) The relative intensities of the lines do not change, except for 3 and 7″ which decrease, as the temperature is lowered from 4.2 to 1.5°K. This result implies that all lines originate from the $S = 0$ ground state except for lines 3 and 7″ which are transitions from the $S = 1$ state. (b) The spectrum of a crystal with 1.0% rhenium shows only a faint line corresponding to line 7 of Fig. 2.

The energy spectrum of the excited state may be calculated from an anisotropic exchange Hamiltonian of the form $\mathcal{H} = -2J_x{}'s_{x1}s_{x2} - 2J_y{}'s_{y1}s_{y2} - 2J_z{}'s_{z1}s_{z2}$. The z direction is defined as the line joining two rhenium ions, which in the K_2PtCl_6 structure is a (110) or equivalent direction. The parameters $J_x{}' = -9.24\ \mathrm{cm}^{-1}$, $J_y{}' = -3.08\ \mathrm{cm}^{-1}$, $J_z{}' = -0.61\ \mathrm{cm}^{-1}$, and the ground-state parameters ob-

Table I. The observed energies of the *o*-*o* and ν_3 absorptions corresponding to the transitions $^4A_{2g}$ (Γ_8) to $^2T_{2g}$ (Γ_7) of Re^{+4} in K_2PtCl_6 at 4.2°K. The wave functions given for the ν_3 transition are those given by the vector coupling of $s_1 = \frac{3}{2}$ and $s_2 = \frac{1}{2}$, with the notation being $|S, M_S\rangle$.

No.	Observed energy (cm^{-1})	$\Delta E = E_1 - E_i$ (cm^{-1})	ΔE(calc) (cm^{-1})	Assignment $S-S'$	Excited-state wave function
			o-*o* transition		
1	13 863.77	0	0	pair 0-2	
2	13 860.92	2.65	2.64	pair 0-1	
3	13 858.50	5.27	5.83	pair 1-2	
4	13 855.20	8.57	8.47	pair 1-1	
5	13 846.56	17.21	17.49	pair 2-2	
6	13 840.81	22.96	22.85	single ion	
	$J = -2.91\ \mathrm{cm}^{-1}$				$J' = -0.66\ \mathrm{cm}^{-1}$
			ν_3 transition		
1	14 182.26	0	$\begin{cases} 0 \\ 0.13 \end{cases}$		$0.255\|1\rangle + 0.931\|2\rangle - 0.255\|4\rangle$ $0.076\|5\rangle - 0.076\|6\rangle + 0.703\|7\rangle + 0.703\|8\rangle$
2	14 177.71	4.55	6.06		$-0.268\|5\rangle - 0.268\|6\rangle + 0.654\|7\rangle - 0.654\|8\rangle$
3	14 175.34	6.92			From $S = 1$ ground state to level 1
4	14 169.71	12.55	12.66		$0.666\|1\rangle + 0.338\|3\rangle - 0.665\|4\rangle$
5	14 165.72	16.54	16.61		$0.659\|1\rangle - 0.361\|2\rangle + 0.659\|4\rangle$
5′			21.97		$0.703\|5\rangle - 0.703\|6\rangle - 0.076\|7\rangle - 0.076\|8\rangle$
6	14 160.00	22.26	35.95		Single ion
7	14 154.75	27.51	28.24		$0.654\|5\rangle + 0.654\|6\rangle + 0.268\|7\rangle - 0.268\|8\rangle$
7′	14 153.91	28.35	28.34		$-0.239\|1\rangle + 0.941\|3\rangle + 0.239\|4\rangle$
7″	14 152.38	29.88			From $S = 1$ to level 5′
	$J_x' = -9.24\ \mathrm{cm}^{-1}$		$J_y' = -3.08\ \mathrm{cm}^{-1}$		$J_z' = -0.61\ \mathrm{cm}^{-1}$
	$\|1\rangle = \|22\rangle$	$\|3\rangle = \|10\rangle$		$\|5\rangle = \|11\rangle$	$\|7\rangle = \|2\bar{1}\rangle$
	$\|2\rangle = \|20\rangle$	$\|4\rangle = \|2\bar{2}\rangle$		$\|6\rangle = \|1\bar{1}\rangle$	$\|8\rangle = \|21\rangle$

tained above give the calculated energies listed in Table I. The rms deviation from the observed energies is 0.24 cm^{-1}. The most intense lines are those with $\Delta M_S = 0, \pm 2$.

The difference of 13.69 cm^{-1} between the calculated and observed energy of the free ion results from a change in the vibration frequency ν_3 associated with the pair relative to that of the single ion. The frequency associated with the pair is 4.3% higher than that associated with the single ion. This change in ν_3 is close to that calculated from the reduced mass ratios of a Re-Re pair and a Re-Pt pair.

To verify the assignments given in Table I, the Zeeman effect on the spectrum was studied at $T = 1.5$°K with the magnetic field parallel to the (111) direction of the crystal. The densitometer tracings for the *o*-*o* transition are shown in Figs. 1(c) and 1(d) for $H = 5$ and 10 kG. Although resolved spectra are not obtained, it is apparent that the broadening is that expected if the lines are transitions from an $S = 0$ to $S = 2$ and $S = 1$ excited states, and $g' = -1.7$.[3] The ν_3 transition pair spectra show broadening also, but no further information could be obtained.

The results of this analysis show that (1) the coupling of rhenium pairs in K_2PtCl_6 crystals in the ground state is antiferromagnetic, and (2) the excited-state coupling parameters are strongly dependent upon the associated vibrational states but are predominantly antiferromagnetic.

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[3] The analysis of the single-ion optical spectra for the other transitions will be reported elsewhere: P. B. Dorain and R. G. Wheeler, to be published.

[4] J. C. Eisenstein, J. Chem. Phys. 34, 1628 (1961).